

## 云木香化学成分研究 I

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**摘要** 从云南丽江产云木香(*Saussurea lappa* C. B. Clarke)的根中分离得到了14个倍半萜化合物, 它们的结构通过波谱和化学的方法得到鉴定。其中化合物2被鉴定为是一新化合物, 化合物4, 12和14为首次从该植物中分离得到。

**关键词** 云木香, 菊科, 倍半萜, 倍半萜内酯, 倍半萜内酯甙

## STUDY ON CHEMICAL CONSTITUENTS OF SAUSSUREA LAPPA I

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**Abstract** The roots of *S. lappa* C. B. Clarke afforded in addition to thirteen sesquiterpenoid constituents (1 and 3~14) reported a new sesquiterpene aldehyde (2). The structure of the new compound was established by spectral method. Moreover, among the thirteen known sesquiterpenoid constituents, Compound 4, 12 and 14 have been obtained from this plant source for the first time.

**Key words** *Saussurea lappa*, Compositae, Sesquiterpenes, Sesquiterpene lactones, Sesquiterpene glycosides

*S. lappa* (Chinese name: Yunmuxiang, Guangmuxiang and Qingmuxiang) introduced from India has been cultivated in Southwest China. It has been a traditional Chinese medicine and also an important spice since ancient time. It possesses the function of spasmolysis, antihypertension and antibacteria(江苏新医学院编著, 1979). Its chemical constituents have been studied by some groups. The main chemical constituents of this plant are sesquiterpenes and sesquiterpene lactones. And many other types of compounds have been reported from this plant(Connoll *et al.*, 1991). However, up to now, the chemical constituents of water soluble fraction of this plant haven't been reported. In order to clarify the medical value of *S. lappa* and to search for biologically active compounds, this study have reinvestigated the chemical constituents of this plant.

From the liposoluble and water soluble fractions of the roots of *S. lappa*, a new sesquiterpene aldehyde,

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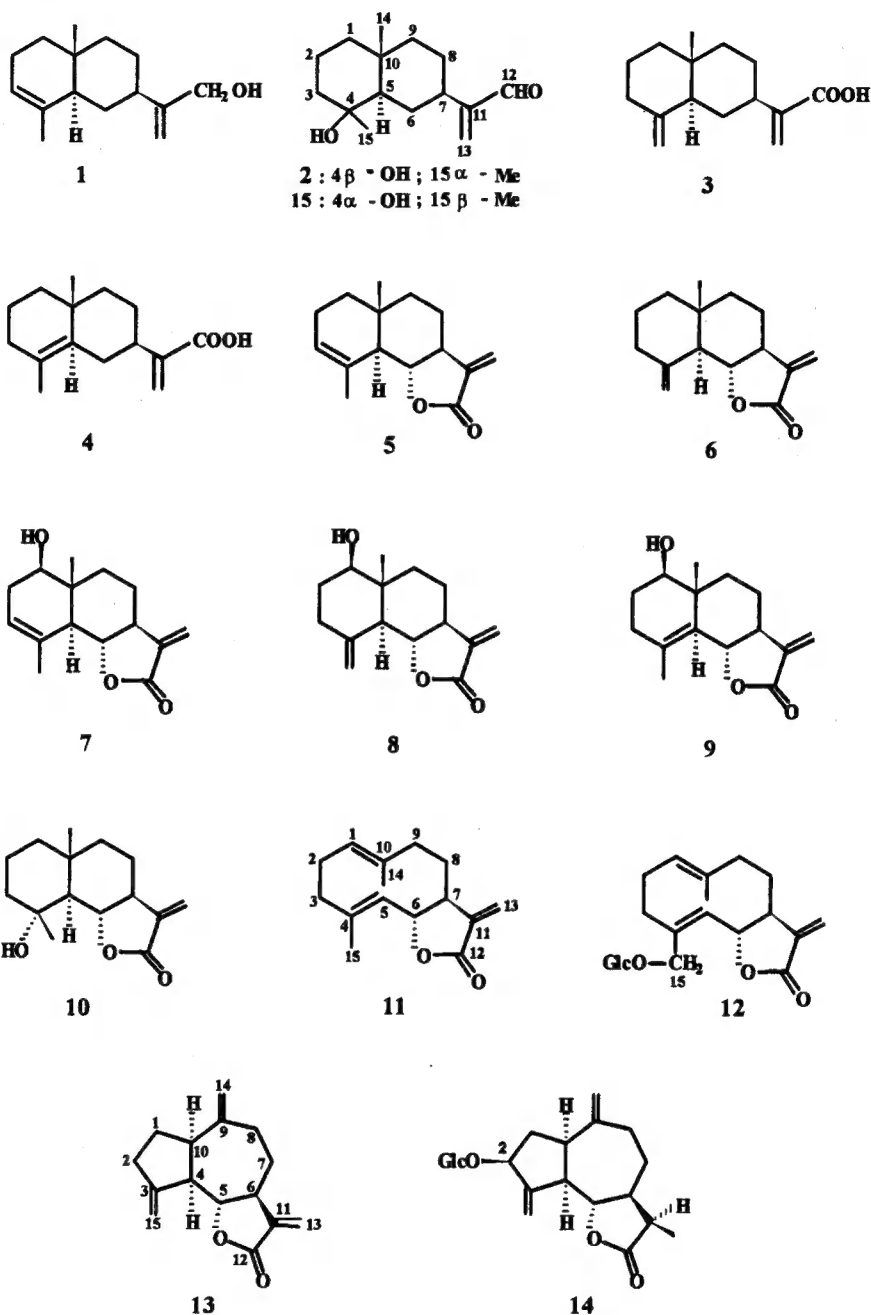
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namely 4 $\beta$ -hydroxy-11(13)-eudesmene-12-al (**2**), has been isolated, in addition to nine sesquiterpenoids with eudesmane skeleton,  $\alpha$ -costol(**1**)(Maurer *et al*, 1977),  $\beta$ -costic acid (**3**)(Bawdekar *et al*, 1965), isocostic acid (**4**)(Cruz *et al*, 1982),  $\alpha$ -cyclocostunolide (**5**),  $\beta$ -cyclocostunolide (**6**)(Govindan *et al*, 1977), santamarine (**7**), reynosin (**8**)(Yoshioka *et al*, 1970), magnolialide (**9**)(El-Feraly *et al*, 1979) and arbusculin A (**10**)(Irwin *et al*, 1969), one germacranolide and its glycoside, costunolide (**11**)(Grieco *et al*, 1977), and costunolide-15- $\beta$ -D-glucopyranoside (**12**)(Bohlmann *et al*, 1977), one guaianolide and its glycoside, dehydrocostus lactone (**13**)(Dhilion *et al*, 1987; Mathur *et al*, 1965), and 11 $\beta$ ,13-dihydroglucozaluzanin C (**14**)(Nishimura *et al*, 1986), and their structures have been elucidated by spectrum analyses.

## RESULTS AND DISCUSSION

**Compound (2)** displayed strong IR absorption bands at 3 600, 1 170  $\text{cm}^{-1}$ , which suggested the presence of a hydroxyl group, an end vinyl group (1 640, 890  $\text{cm}^{-1}$ ) and an aldehyde group (2 705, 1 690  $\text{cm}^{-1}$ ). The mass spectrum (EI) showed a molecular ion peak at  $m/z$  236, which agreed with a molecular formula  $\text{C}_{15}\text{H}_{24}\text{O}_2$ . This conclusion was supported by its  $^{13}\text{C}$  NMR and DEPT spectra (Table 1). The  $^1\text{H}$  NMR spectrum had two singlets at  $\delta$ 1.06 (H-14) and 1.15 (H-15) assigned to tertiary methyl groups, the latter having an oxygenated function at the  $\beta$ -position; a singlet at 9.51 (1H, -CHO) and two singlets at 5.69 and 6.29 (each 1H, terminal vinyl group, H-13). These data gave the clue to the structure of the product, as it was very similar to that of 4 $\alpha$ -hydroxy-11(13)-eudesmene-12-al (**15**)(Guerreiro *et al*, 1979), which was an artifact product obtained by oxidation of 4 $\alpha$ -hydroxy-11(13)-eudesmene-12-ol(Guerreiro *et al*, 1979). If comparing the  $^1\text{H}$  NMR spectral data of **2** with those of **15**, apparently, the main difference between them resided in the position of the 14-Me and 15-Me respectively, which were at the lower field in the spectrum of **2** [the corresponding signals in the spectrum of **15** were at  $\delta$ 0.88 (H-14) and 1.04 (H-15)]. These facts could be explained by assigning both compounds epimeric 11(13)-eudesmene-12-al structures with one additional OH group at C-4 $\beta$ (**2**) or C-4 $\alpha$ (**15**) position respectively. The conclusion was also confirmed by comparison of NMR spectra of **2** with those of the methyl ester of ilicic acid (4 $\alpha$ -hydroxyl-11(13)-eudesmene-12-oic acid)(**16**)(Sanz *et al*, 1990). In addition to the difference of their  $^1\text{H}$  NMR spectra data of H-14 and H-15 [the corresponding signals are at the  $\delta$ 0.90(s, H-14) and 1.10 (s, H-15) in **16**], the presence of 4 $\beta$ -OH in **2** was supported by the low fieldshift of C-15 ( $\delta$ 30.30, q) and upshift of C-2 ( $\delta$ 18.10, t)[the corresponding signals are at the  $\delta$ 22.45 (C-15,q) and 20.12 (C-2, t)in **16**] due to the disappearance of the 1,3 - compressed effect between C-14 and C-15, and the stronger  $\gamma$ - gauche shielding effect between 4 $\beta$ -OH and C-2 respectively. Therefore, compound **2** was characterized as 4 $\beta$ -hydroxy-11(13)-eudesmene-12-al.

The structures of the thirteen known sesquiterpenoid constituents were identified on the basis of physical constants and spectral data. According to our investigation, the main chemical constituents of this plant were sesquiterpenes and sesquiterpene lactones. This conclusion agreed with the previous researches. However, it must be emphasized that the above compounds except for compound **11** and **13** occur in the roots of *S. lappa* only in trace amounts.



## EXPERIMENT

**Mp** uncorr.; **MS**: 70 eV; **NMR**:  $^1\text{H}$  at 400 MHz,  $^{13}\text{C}$  at 100 MHz. The multiplicities of  $^{13}\text{C}$  NMR spectral data were determined with the aid of 1 D Distortionless Enhancement Polarization Transfer (DEPT) spectra.

**Plant material** *S. lappa* C. B. Clarke was produced in Lijiang, Yunnan, China. Research samples were

obtained from Yunnan Native Products Branch, National Import & Export Corporation of Native & Animal Products of China.

**Extraction and isolation** The air-dried powdered roots (2.5 kg) of *S. lappa* were extracted with Et<sub>2</sub>O (5 × 4000 mL) at room temperature during 3 weeks. The extract was evapd. to dryness in vacuo and the residue (142.0 g) was chromatographed on a silica gel column (200~300 mesh, 470.0 g, 120 × 4 cm) and successively eluted with petrol-ether (1:0, 9:1, 3:1, 1:1 and 0:1) to give frs. A (20.2 g), B (82.7 g), C (6.5 g), D (6.8 g) and E (5.5 g). From fr. A, β-costic acid (3) (57 mg), isocostic acid (4) (36 mg) and α-cyclocostunolide (5) (75 mg), and from fr. B, α-costol (1) (33 mg), β-cyclocostunolide (6) (8 mg), costunolide (11) (12.0 g), and dehydrocostus lactone (13) (8.0 g) were obtained by CC on silica gel (or silica gel impregnated with silver nitrate) eluting with petrol-ether and petrol-chloroform, respectively. Frs. C and D were chromatographed on medium pressure column developing with petrol-ether, petrol-chloroform and petrol-acetone to yield 4β-hydroxy-11(13)-eudesmene-12-al (2) (6 mg), santamarine (7) (80 mg), reynosin (8) (323 mg), magnolialide (9) (27 mg) and arbusculin A (10) (156 mg).

After being extracted with Et<sub>2</sub>O, the same powdered roots were air-dried again and then were extracted with CH<sub>3</sub>OH (6 × 4000 mL) at room temperature during 4 weeks to give 235.0 g crude extract. The extract was suspended in H<sub>2</sub>O and then successively fractionated with n-BuOH. After the removal of solvent by evapn., the residue (63.0 g) was subjected to CC over silica gel eluting with AcOEt to furnish frs. X<sub>1</sub> (0.6 g), X<sub>2</sub> (2.5 g), X<sub>3</sub> (2.6 g), X<sub>4</sub> (0.8 g). Fr. X<sub>2</sub> was purified by a column on Lobar RP-8 with 50% MeOH to yield costunolide-15-β-D-glucopyranoside (12) (251 mg) and 11β,13-dihydroglucozaluzanin C (14) (74 mg).

**α-costol (1)** C<sub>15</sub>H<sub>24</sub>O, colourless oil, [α]<sub>D</sub><sup>25</sup>+32.6° (CHCl<sub>3</sub>; c 4.3). IR<sub>v</sub><sub>max</sub>cm<sup>-1</sup>: 3 400, 3 085, 2 960, 1 640, 1 440, 1 368, 1 170, 1 020, 895; EIMS (70 eV, m/z (%)): 220(42)[M]<sup>+</sup>, 202(22), 187(53), 173(19), 161(48), 145(52), 131(49), 119(57), 105(88), 91(100), 79(75), 67(55), 55(69); <sup>1</sup>H NMR (400 Hz, CDCl<sub>3</sub>): δ 5.28(1H, m, H-3), 5.01(1H, br.s, H-13a), 4.90(1H, br.s, H-13b), 4.09(2H, br.d, J=6.3Hz, H-12), 1.54(3H, br.s, H-15), 0.82(3H, s, H-14); <sup>13</sup>C NMR data see Table 1.

**4β-hydroxy-11(13)-eudesmene-12-al(2)** C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>, colourless oil, [α]<sub>D</sub><sup>13.7</sup>+45.8° (CHCl<sub>3</sub>; c 0.267); IR<sub>v</sub><sub>max</sub>cm<sup>-1</sup>: 3 600, 3 530, 2 965, 2 705, 1 740, 1 690, 1 660, 1 640, 1 450, 1 380, 1 240, 1 170, 1 140, 960, 890, 870, 810; EIMS(70eV, m/z (%)): 236(4)[M]<sup>+</sup>, 221(37), 203(13), 185(6), 175(9), 159(10), 149(12), 133(21), 109(25), 95(40), 81(43), 71(68), 55(100); <sup>1</sup>H NMR (400 Hz, CDCl<sub>3</sub>): δ 9.51(1H, s, H-12), 6.29(1H, s, H-13a), 5.69(1H, s, H-13b), 1.15(3H, s, H-15), 1.06(3H, s, H-14); <sup>13</sup>C NMR data see Table 1.

**β-costic acid (3)** C<sub>15</sub>H<sub>22</sub>O<sub>2</sub>, colourless needles(EtOH), mp 86~87.5°C, [α]<sub>D</sub><sup>25</sup>+23.4° (CHCl<sub>3</sub>; c 3.0); IR<sub>v</sub><sub>max</sub>cm<sup>-1</sup>: 3 400, 3 035, 2 960, 1 750, 1 630, 1 430, 1 245, 1 140, 885, 750; EIMS(70eV, m/z (%)): 234(13)[M]<sup>+</sup>, 219(12), 216(33), 201(30), 187(54), 161(50), 145(51), 131(49), 119(56), 105(90), 91(100), 79(75), 67(55), 55(70); <sup>1</sup>H NMR (400 Hz, CDCl<sub>3</sub>): δ 6.28(1H, s, H-13a), 5.65(1H, s, H-13b), 4.67(1H, d, J=1.5Hz, H-15a), 4.37(1H, d, J=1.5Hz, H-15b), 0.70(3H, s, H-14); <sup>13</sup>C NMR data see Table 1.

**Isocostic acid (4)** C<sub>15</sub>H<sub>22</sub>O<sub>2</sub>, colourless oil, IR<sub>v</sub><sub>max</sub>cm<sup>-1</sup>: 3 550~3 000, 2 980, 1 695, 1 650, 1 460, 1 380, 1 355, 1 230, 1 150, 870; EIMS(70eV, m/z (%)): 234(69)[M]<sup>+</sup>, 219(81), 205(10), 189(30), 177(19), 161(16), 145(17), 138(23), 121(26), 105(37), 95(100), 79(74), 67(36), 55(65); <sup>1</sup>H NMR (400 Hz, CDCl<sub>3</sub>): δ 6.27(1H, d, J=1.5Hz, H-13a), 5.65(1H, d, J=1.5Hz, H-13b), 1.52(3H, s, H-15), 0.89(3H, s, H-14); <sup>13</sup>C NMR data see Table 1.

Table 1 <sup>13</sup>C NMR Data and DEPT Spectrum of 1~10 in CDCl<sub>3</sub>(100 MHz, δ, from TMS)

C	1	2	3	4	5	6	7	8	9	10
1	40.22t	41.62t	41.81t	42.13t	39.07t	41.87t	75.17d	78.26d	77.32d	40.97t
2	22.87t	18.10t	23.41t	28.78t	22.68t	21.71t	32.80t	31.38t	26.78t	19.35t
3	120.96d	43.82t	41.05t	40.23t	122.40d	39.79t	121.32d	33.56t	38.04t	42.86t
4	154.18s	71.89s	145.31s	134.34s	132.78s	144.44s	133.41s	142.50s	128.98s	71.55s
5	46.88d	51.92d	49.87d	133.05s	51.12d	55.10d	51.21d	53.09d	126.16s	57.90d
6	27.37t	26.72t	27.40t	29.69t	82.40d	80.10d	81.51d	79.59d	83.18d	81.46d
7	42.41d	37.12d	39.41d	37.03d	51.35d	50.06d	51.04d	49.67d	49.64d	50.73d
8	29.31t	27.14t	29.95t	32.44t	21.34t	22.91t	21.18t	21.49t	22.92t	21.91t
9	37.82t	41.54t	36.78t	36.76t	37.61t	36.01t	34.32t	35.81t	33.13t	40.07t
10	32.24s	33.82s	35.85s	34.45s	35.85s	38.69s	40.88s	43.00s	41.91s	37.56s
11	134.79s	155.41s	150.53s	147.17s	139.28s	139.72s	139.08s	139.40s	138.50s	138.53s
12	65.07 t	194.50d	172.18s	172.65s	171.27s	170.67s	170.96s	170.51s	170.90s	169.70s
13	107.80t	132.68t	124.56t	124.50t	116.33t	116.50t	116.58t	116.63t	118.38t	117.51t
14	15.54q	18.74q	16.32q	13.06q	17.14q	18.06q	11.03q	11.64q	18.28q	19.71q
15	20.99q	30.30q	105.42t	14.09q	23.26q	109.19t	23.19q	110.58t	19.37q	24.16q

Table 2 <sup>13</sup>C NMR Data and DEPT Spectrum of 11~14 in CDCl<sub>3</sub>(\* in C<sub>5</sub>D<sub>5</sub>N)(100 MHz, δ, from TMS)

C	11	12 *	13	14 *	C	11	12 *	13	14 *
1	127.05d	126.89d	30.27t	44.97t	12	170.26s	170.32s	170.04s	179.21s
2	28.10t	27.73t	36.10t	80.12d	13	119.36t	119.18t	119.86t	17.03d
3	40.99t	41.17t	149.21s	152.39s	14	16.01q	16.22q	109.55t	109.53t
4	140.19s	141.02s	52.06d	53.28d	15	17.23q	67.78t	112.57t	114.54t
5	127.35d	130.18d	85.06d	84.40d	Glc1'		105.32d		105.54d
6	81.84d	80.33d	47.70d	41.65d	2'		75.21d		75.56d
7	50.45d	50.80d	30.90t	30.22t	3'		78.40d		78.47d
8	26.14t	27.14t	32.57t	32.62t	4'		71.78d		71.87d
9	39.44t	35.95t	139.89s	145.66s	5'		78.63d		79.07d
10	136.83s	137.62s	45.16d	47.84d	6'		62.93t		63.06t
11	141.27s	141.24s	151.14s	54.67d					

**α-cyclocostunolide (5)** C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>, colourless needles (MeOH), mp 81~83℃, [α]<sub>D</sub><sup>24</sup>+115° (CHCl<sub>3</sub>; c 1.10); IRν<sub>max</sub><sup>KBr</sup>cm<sup>-1</sup>: 2 950, 1 755, 1 665, 1 440, 1 254, 1 138, 980, 920, 845; EIMS(70eV, m/z (%)): 232(80) [M]<sup>+</sup>, 217(100), 203(16), 189(20), 171(21), 163(46), 149(74), 135(22), 119(39), 107(60), 91(72), 79(53), 67(43); <sup>1</sup>H NMR(400Hz, CDCl<sub>3</sub>): δ6.03(1H, d, J=3.2Hz, H-13a), 5.36(1H, d, J=3.2Hz, H-13b), 5.35(1H, br.s, H-3), 3.84(1H, t, J=11.0Hz, H-6β), 1.80(3H, br.s, H-15), 0.87(3H, s, H-14); <sup>13</sup>C NMR data see Table 1.

**β-cyclocostunolide (6)** C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>, colourless needles (Et<sub>2</sub>O), mp 68~70℃; [α]<sub>D</sub><sup>27</sup>+170° (CHCl<sub>3</sub>); IRν<sub>max</sub><sup>KBr</sup>cm<sup>-1</sup>: 2 960, 1 753, 1 635, 1 435, 1 240, 1 120, 880; EIMS(70eV, m/z (%)):232(100) [M]<sup>+</sup>, 217(67), 204(14), 189(33), 175(25), 163(81), 149(53), 135(34), 121(35), 107(41), 91(67), 79(62), 67(48); <sup>1</sup>H NMR (400 Hz, CDCl<sub>3</sub>): δ6.05 (1H, d, J=3.1Hz, H-13a), 5.38 (1H, d, J=3.1Hz, H-13b), 4.91 (1H, br.s, H-15a), 4.77 (1H, br.s, H-15b), 3.94(1H, t, J=10.9Hz, H-6β), 0.82(3H, s, H-14); <sup>13</sup>C NMR data see Table 1.

**Santamarine (7)** C<sub>15</sub>H<sub>20</sub>O<sub>3</sub>, colourless needles(Me<sub>2</sub>CO), mp 137~139℃; [α]<sub>D</sub><sup>20</sup>+95.8° (CHCl<sub>3</sub>; c 0.50); UVλ<sub>max</sub><sup>MeOH</sup>nm : 239, 288; IRν<sub>max</sub><sup>KBr</sup>cm<sup>-1</sup>: 3 380, 2 940, 1 752, 1 653, 1 430, 1 335, 1 260, 1 128, 1 038, 970, 950, 845; EIMS(70eV, m/z (%)): 248(95) [M]<sup>+</sup>, 230(39), 215(16), 204(31), 191(32), 175(29), 163(53), 152(83),

145(35), 133(42), 107(100), 91(79), 81(66), 67(50), 55(85);  $^1\text{H}$  NMR (400Hz,  $\text{CDCl}_3$ ):  $\delta$ 6.03(1H, d,  $J=3.2\text{Hz}$ , H-13a), 5.37(1H, d,  $J=3.2\text{Hz}$ , H-13b), 5.31(1H, br.s, H-3), 3.91(1H, t,  $J=11.0\text{Hz}$ , H-6 $\beta$ ), 3.63(1H, dd,  $J=9.9, 6.6\text{Hz}$ , H-1 $\alpha$ ), 1.79(3H, br.s, H-15), 0.84(3H, s, H-14);  $^{13}\text{C}$  NMR data see Table 1.

**Reynosin (8)**  $\text{C}_{15}\text{H}_{20}\text{O}_3$ , white powder ( $\text{Me}_2\text{CO}$ ), mp  $145\sim 146^\circ\text{C}$ ;  $[\alpha]_{\text{D}}^{25}+178^\circ$  (EtOH;  $c$  0.15);  $\text{IR}_{\text{max}}^{\text{KBr}}\text{cm}^{-1}$ : 3 400, 2 955, 1 750, 1 646, 1 410, 1 326, 1 254, 1 150, 950, 840; EIMS(70eV,  $m/z$  (%)): 248(6)  $[\text{M}]^+$ , 230(100), 215(9), 204(10), 189(8), 175(11), 163(78), 149(23), 133(18), 119(24), 105(31), 91(46), 79(38), 67(27), 55(40);  $^1\text{H}$  NMR(400Hz,  $\text{CDCl}_3$ ):  $\delta$ 5.99(1H, d,  $J=3.2\text{Hz}$ , H-13a), 5.34(1H, d,  $J=3.2\text{Hz}$ , H-13b), 4.89(1H, br.s, H-15a), 4.76(1H, br.s, H-15b), 3.95(1H, t,  $J=10.8\text{Hz}$ , H-6 $\beta$ ), 3.44(1H, dd,  $J=7.6, 4.3\text{Hz}$ , H-1 $\alpha$ ), 0.73(3H, s, H-14);  $^{13}\text{C}$  NMR data see Table 1.

**Magnolialide (9)**  $\text{C}_{15}\text{H}_{20}\text{O}_3$ , colourless needles ( $\text{Me}_2\text{CO}$ ), mp  $151\sim 153^\circ\text{C}$ ;  $[\alpha]_{\text{D}}^{25}+74^\circ$  (EtOH;  $c$  0.23);  $\text{UV}_{\text{max}}^{\text{MeOH}}\text{nm}$ : 239, 288;  $\text{IR}_{\text{max}}^{\text{KBr}}\text{cm}^{-1}$ : 3 380, 2 940, 1 752, 1 653, 1 430, 1 335, 1 260, 1 128, 1 038, 1 000, 970, 950, 845; EIMS(70eV,  $m/z$  (%)): 248(95)  $[\text{M}]^+$ , 230(39), 215(16), 204(31), 191(32), 175(29), 163(53), 152(83), 145(35), 133(42), 107(100), 91(79), 81(66), 67(49), 55(89);  $^1\text{H}$  NMR (400Hz,  $\text{CDCl}_3$ ):  $\delta$ 6.07(1H, d,  $J=3.2\text{Hz}$ , H-13a), 5.42(1H, d,  $J=3.2\text{Hz}$ , H-13b), 4.51(1H, br.d,  $J=10.0\text{Hz}$ , H-6 $\beta$ ), 3.44(1H, dd,  $J=11.3, 4.5\text{Hz}$ , H-1 $\alpha$ ), 1.75(3H, br.s, H-15), 1.01(3H, s, H-14);  $^{13}\text{C}$  NMR data see Table 1.

**Arbusculin A (10)**  $\text{C}_{15}\text{H}_{22}\text{O}_3$ , colourless cryst. ( $\text{Et}_2\text{O}$ ), mp  $76\sim 77.5^\circ\text{C}$ ;  $[\alpha]_{\text{D}}^{24}+25.8^\circ$  ( $\text{CHCl}_3$ ;  $c$  4.2);  $\text{IR}_{\text{max}}^{\text{KBr}}\text{cm}^{-1}$ : 3 578, 3 082, 2 930, 1 758, 1 660, 1 450, 1 380, 1 356, 1 320, 1 288, 1 272, 1 244, 1 215, 1 174, 1 140, 1 030, 960, 870; EIMS(70eV,  $m/z$  (%)): 250(11)  $[\text{M}]^+$ , 235(100), 217(56), 204(44), 189(49), 171(27), 165(64), 147(56), 131(24), 119(78), 109(35), 91(46), 81(51), 55(69);  $^1\text{H}$  NMR(400Hz,  $\text{CDCl}_3$ ):  $\delta$ 6.06(1H, d,  $J=3.1\text{Hz}$ , H-13a), 5.40(1H, d,  $J=3.1\text{Hz}$ , H-13b), 3.99(1H, t,  $J=11.2\text{Hz}$ , H-6 $\beta$ ), 1.29(3H, s, H-15), 0.93(3H, s, H-14);  $^{13}\text{C}$  NMR data see Table 1.

**Costunolide (11)**  $\text{C}_{15}\text{H}_{20}\text{O}_2$ , colourless cryst. (MeOH), mp  $106\sim 107^\circ\text{C}$ ;  $[\alpha]_{\text{D}}^{20}+128^\circ$  ( $\text{CHCl}_3$ ;  $c$  0.45);  $\text{IR}_{\text{max}}^{\text{KBr}}\text{cm}^{-1}$ : 2 980, 1 750, 1 652, 1 430, 1395, 1 375, 1 305, 1 280, 1 240, 1 190, 1 050, 962, 890, 808; EIMS(70eV,  $m/z$  (%)): 232(70)  $[\text{M}]^+$ , 217(60), 204(41), 189(62), 175(88), 149(87), 122(100), 107(89), 95(96), 83(47), 77(67), 65(71), 51(61), 39(79);  $^1\text{H}$  NMR (400Hz,  $\text{CDCl}_3$ ):  $\delta$ 6.22(1H, d,  $J=3.5\text{Hz}$ , H-13a), 5.49(1H, d,  $J=3.5\text{Hz}$ , H-13b), 4.80(1H, dd,  $J=10.5, 4.3\text{Hz}$ , H-1), 4.69(1H, br.d,  $J=9.9\text{Hz}$ , H-5), 4.53(1H, t,  $J=9.3\text{Hz}$ , H-6), 1.67(3H, s, H-15), 1.36(3H, s, H-14);  $^{13}\text{C}$  NMR data see Table 2.

**Costunolide-15- $\beta$ -D-glucopyranoside (12)**  $\text{C}_{21}\text{H}_{30}\text{O}_8$ , amorphous white powder,  $[\alpha]_{\text{D}}^{27.9}+26.67^\circ$  (MeOH;  $c$  0.478);  $\text{UV}_{\text{max}}^{\text{MeOH}}\text{nm}$ : 241.5;  $\text{IR}_{\text{max}}^{\text{KBr}}\text{cm}^{-1}$ : 3 700~3 000, 2 920, 1 750, 1 650, 1 435, 1 396, 1 280, 1 240, 1 070, 960, 890; FABMS ( $m/z$  (%)): 433(4)  $[\text{M}+\text{Na}]^+$ , 411(19)  $[\text{M}+1]^+$ , 249(55), 231(89), 219(15), 203(18), 191(22), 175(34), 159(88), 145(58), 133(38), 119(50), 105(67), 91(82), 81(100), 69(60);  $^1\text{H}$  NMR(400Hz,  $\text{C}_5\text{D}_5\text{N}$ ):  $\delta$ 6.32 (1H, d,  $J=3.4\text{Hz}$ , H-13a), 5.49 (1H, d,  $J=3.4\text{Hz}$ , H-13b), 5.01(1H, dd,  $J=10.0, 4.3\text{Hz}$ , H-1), 4.93 (1H, d,  $J=7.8\text{Hz}$ , H-5), 4.70(1H, t,  $J=7.8\text{Hz}$ , H-6), 4.80(1H, d,  $J=12.0\text{Hz}$ , H-15a), 4.22(1H, d,  $J=12.0\text{Hz}$ , H-15b), 1.34(3H, s, H-14), 4.86(1H, d,  $J=7.7\text{Hz}$ , H-1'), 4.02(1H, t,  $J=8.1\text{Hz}$ , H-2'), 4.23(1H, t,  $J=8.8\text{Hz}$ , H-3'), 4.18(1H, t,  $J=8.8\text{Hz}$ , H-4'), 3.96 (1H, m, H-5'), 4.53 (1H, dd,  $J=11.8, 2.2\text{Hz}$ , H-6'a), 4.37 (1H, dd,  $J=11.8, 5.3\text{Hz}$ , H-6'b);  $^{13}\text{C}$  NMR data see Table 2.

**Dehydrocostus lactone(13)**  $\text{C}_{15}\text{H}_{18}\text{O}_2$ , colourless cryst. ( $\text{Et}_2\text{O}$ ), mp  $60\sim 61.5^\circ\text{C}$ ;  $[\alpha]_{\text{D}}^{25}-20^\circ$  ( $\text{CHCl}_3$ ;  $c$  1.3);  $\text{IR}_{\text{max}}^{\text{KBr}}\text{cm}^{-1}$ : 3 028, 2 950, 1 750, 1 626, 1 454, 1 398, 1 348, 1 318, 1 295, 1 250, 1 125, 1 008, 948, 908, 890, 810; EIMS(70eV,  $m/z$  (%)): 230(64)  $[\text{M}]^+$ , 215(15), 201(27), 185(13), 173(18), 150(69), 129(19), 119(27), 105(44), 82(100), 65(23), 53(55), 41(47);  $^1\text{H}$  NMR(400Hz,  $\text{CDCl}_3$ ):  $\delta$ 6.18(1H, d,  $J=3.3\text{Hz}$ , H-13a), 5.46(1H, d,  $J=3.3\text{Hz}$ , H-13b), 5.23(1H, br.s, H-15a), 5.02(1H, br.s, H-15b), 4.86(1H, br.s, H-14a),

4.77(1H, br.s, H-14b), 3.92(1H, t,  $J=9.2\text{Hz}$ , H-5),  $^{13}\text{C}$  NMR data see Table 2.

**11 $\beta$ ,13-dihydroglucozaluzanin C(14)**  $\text{C}_{21}\text{H}_{30}\text{O}_8$ , amorphous white powder,  $[\alpha]_{\text{D}}^{27.7}+6.12^\circ$  (MeOH;  $c$  0.449);  $\text{UV}\lambda_{\text{max}}^{\text{MeOH}}$  nm: 241, 280, 315;  $\text{IR}\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 3 600~3 100, 2 910, 1 750, 1 630, 1352, 1070, 890; FABMS ( $m/z(\%)$ ): 433(4)  $[\text{M}+\text{Na}]^+$ , 411(19)  $[\text{M}+1]^+$ , 249(30), 231(80), 203(17), 189(12), 175(18), 157(69), 145(58), 133(100), 119(39), 105(51), 91(68), 69(67);  $^1\text{H}$  NMR(400Hz,  $\text{C}_5\text{D}_5\text{N}$ ):  $\delta$ 5.35(1H, br.s, H-15a), 5.07(1H, br.s, H-15b), 5.10(1H, br.s, H-14a), 4.84(1H, br.s, H-14b), 3.99(2H, m, H-2,5), 1.81(3H, d,  $J=7.0\text{Hz}$ , H-13), 5.00(1H, d,  $J=7.8\text{Hz}$ , H-1'), 3.99(2H, m, H-2',5'), 4.22(2H, m, H-3', 4'), 4.37(1H, dd,  $J=15.6, 5.5\text{Hz}$ , H-6'a), 4.57(1H, dd,  $J=15.6, 2.3\text{Hz}$ , H-6'b);  $^{13}\text{C}$  NMR data see Table 2.

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